pH control as a tool for the synthesis of Ag Nanoparticles (NPs) aggregates with plasmonic applications

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INTRODUCTION

The degree of aggregation of nanoparticles (NPs) exerts an important influence on the physicochemical properties of a dispersion, like optical absorption and photothermal effect[1]. Hence, the controlled tuning of aggregation can be a valuable tool for the synthesis of NPs systems with specific properties and potential technological applications. The stability and degree of aggregation of Ag NPs in a dispersion depend on the nature of the capping agent and also on the properties of the surrounding medium (pH, ionic strength, polarity, etc.)[2]. In this work, we analysed the effect of pH and concentration on the aggregation of silver NPs, capped with a ligand bearing carboxylic acid groups, in aqueous dispersions. We then determined the effect of the size of these aggregates on the optical absorption and photothermal effect of the dispersions.

EXPERIMENTAL METHODS

Ag NPs of approximately 4 nm in diameter, coated with 11-mercaptoundecanoic acid (MUA), were obtained following the procedure developed in our laboratory[3].
From the diluted dispersion of Ag NPs, aggregates were generated by controlling the pH values, adjusting them between values of 3 and 10. This step was carried out by adding diluted solutions of NaOH and HCl and using a pH meter as a control instrument.
The aggregation process and the size of the obtained structures were analysed by UV-Visible spectrophotometry, Dynamic Light Scattering (DLS) and Small Angle X-ray Dispersion (SAXS). In addition, tests were carried out to determine the photothermal effect of NPs and their dependence with the level of aggregation. They consisted in the irradiation of the dispersions with a green laser (532 nm, 1 W), using a thermocouple and thermographic camera to record temperature changes.

RESULTS AND DISCUSSION

At high pH (greater than the pKa of the acid), almost all carboxylic groups that are exposed to the medium (water) are deprotonated and therefore, negatively charged, which makes NPs stable in dispersion due to electrostatic repulsion. When pH is reduced, carboxylate groups are protonated, hydrogen bonding associations appear and aggregates are formed. This process is observed in UV-vis spectra (Fig.1) in which the plasmonic band of NPs broadens and red-shifts with the decrease in pH.

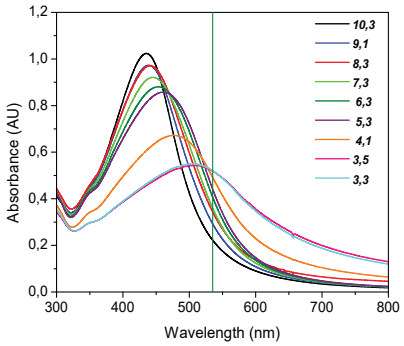

Figure 1. UV-vis spectra for the diluted dispersions of NPs at different pH values.

DLS also shows that a decrease in pH produces an increase in the size of the aggregates. SAXS spectra reveal that the aggregate /unbundled transition is reversible. All the evaluated samples (different pH values) shows photothermal effect at 532 nm, with values of temperature increases as high as 10ºC for very diluted dispersions of Ag NPs. Most importantly, results indicate that the photothermal effect of Ag NPs and their aggregates can be activated with a laser not-centred at the wavelength of the maximum of the silver NPs plasmon band, which is important for application of these dispersions as heating systems.

CONCLUSION

Ag NPs aggregates can be synthesized by controlling pH of Ag NPs dispersions coated with MUA. The formation of these aggregates as a function of the pH is reversible. The size of the aggregates and the increase in temperature induced by photothermal effect depends on the pH of the dispersion. Finally, results show that a total matching between the wavelength of the irradiation source and the position of the plasmon band is not critical for the activation of the photothermal effect.

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